Supporting Material

Thermodynamic Studies of $[H_2Rh(diphosphine)_2]^+$ and $[HRh(diphosphine)_2(CH_3CN)]^{2+}$ Complexes in Acetonitrile

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Derivation of Tolman cone angles. Tolman calculated the cone angle for diphosphine ligands (Θ_B) using equation 1, where Θ_M is the cone angle of the corresponding monodentate PR_3 ligand with the same R substituents as the diphosphine ligands and α is the experimentally observed PMP bond angle of the chelating diphosphine ligand. We have extended this method to the other ligands shown in Chart 1 using the experimentally determined bite angles from the work of Aguila, et. al. and the cone angles for the corresponding monodentate ligands used by Tolman.[2] The cone angle values derived in this way agree very well with the available data from Tolman (values shown in parentheses) and allow a logical extension to the new ligands used in this work.

$$\Theta_B = 2/3(\Theta_M + 1/2\alpha) \qquad (1)$$

Table S1. Data used to calculate Tolman cone angles for bidentate ligands and $\Sigma^3\chi$.

PP	1/2 α (°)[a]	Θ_M (°)[b]	Θ_B (°)[c]	TEM[d] $\Sigma^3\chi$
dppm	**36**	**145**	**121 (121)**	11.2
dmpe	**43**	**118**	**107 (107)**	7.8
depe	**43**	**132**	**117 (115)**	6.2
dppe	**43**	**145**	**125 (125)**	11.2
dcpe	**43**	**170**	**142 (142)**	2.8
depp	**46**	**132**	**119**	6.2
depx	**50**	**132**	**121**	6.2
dppb	**43**	**145**	**125**	12.9
dppp	**46**	**145**	**127 (127)**	11.2

[a] Data from Ref 1. [b]Data from reference 2. [c]Calculated using eq. 1. Values in parenthesis are from ref. 2. [d]The Tolman Electronic Parameters (TEMs, χ) values for substituents were obtained from Ref. 2. The sum (Σ^3) of χ for each phosphine was obtained by adding the values of the two substituents to the values for CH_3 or Ph. The χ values for CH_3 and Ph were used for the alkyl or aryl groups of the diphosphine backbone.

References for Supporting Information

1. Aguila, D.; Escribano, E.; Speed, S.; Talancon, D.;, Yerman, L.; Alvarez, S. *Dalton Trans.* **2009**, 6610-6625**.**

2. Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313-348.